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# Computational Studies of Ionic Liquids

## AFOSR Ionic Liquids Workshop

## March 7-8, 2004

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# *Outline*

1. Introduction
2. Structures and relative energies of 1,5-diamino-1,2,3,4-tetrazolium cation
3. Summary and Conclusions

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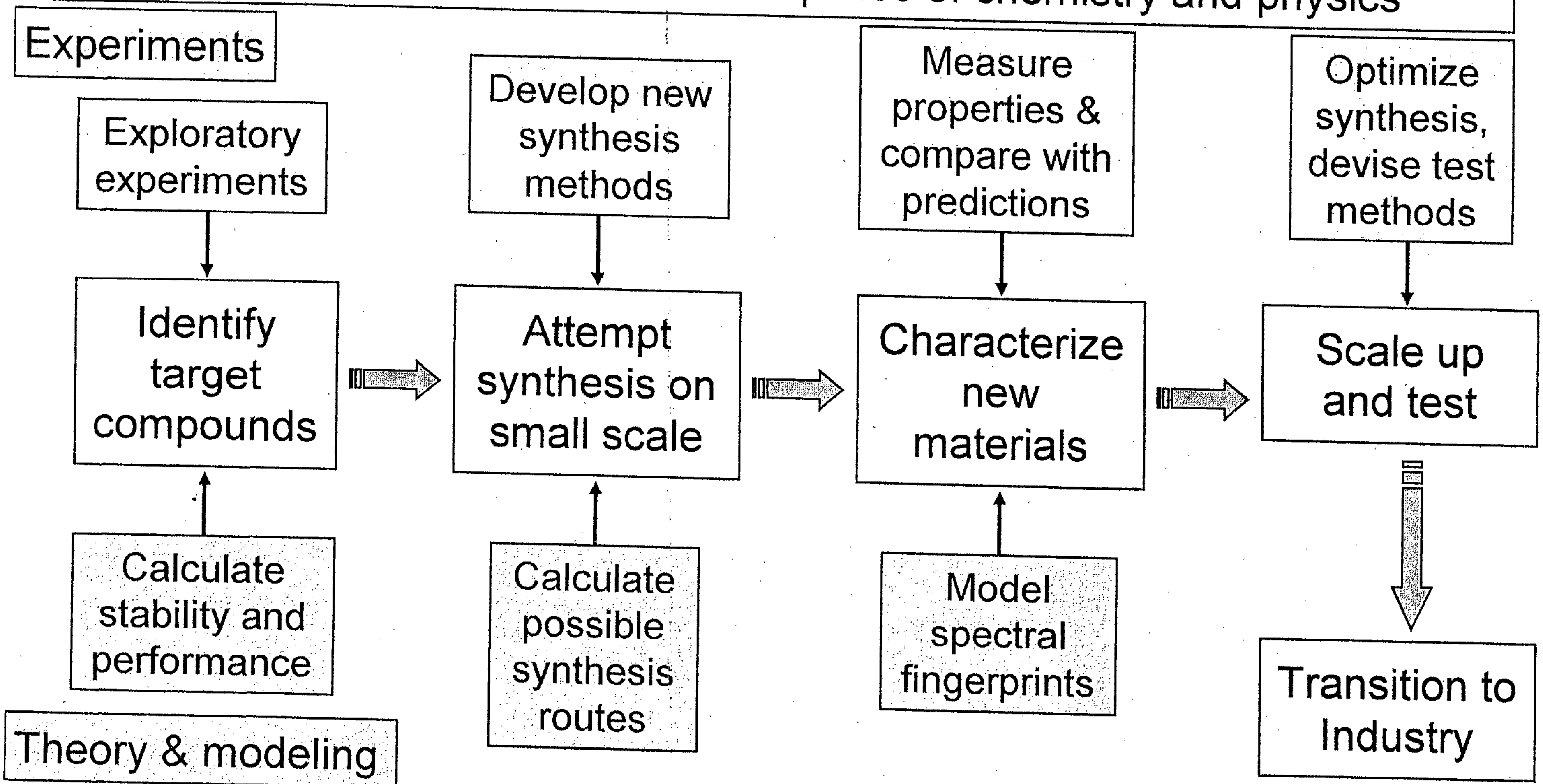
# Propellants Program
# General Approach

Employ a synergic blend of experimental, theoretical, and computational techniques derived from the disciplines of chemistry and physics

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# Modeling & Simulation of New Chemical Propellants

Various computational techniques are employed to solve the molecular electronic Schrödinger equation from quantum mechanics:

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 - \sum_i \sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} + \sum_i \sum_{j>i} \frac{1}{r_{ij}}\right]\Psi_{el} = E_{el}\Psi_{el}$$

**Is a proposed propellant molecule/material stable?**

- Structure optimization, verification as local minimum

**What is its energy content?**

- Heats of formation and combustion

**How may it be synthesized? How will it react/decompose/combust?**

- Reaction pathways

**How will we know if we've synthesized it?**

- Vibrational spectra (IR, Raman, isotopic shifts)
- NMR chemical shifts
- Electronic spectra

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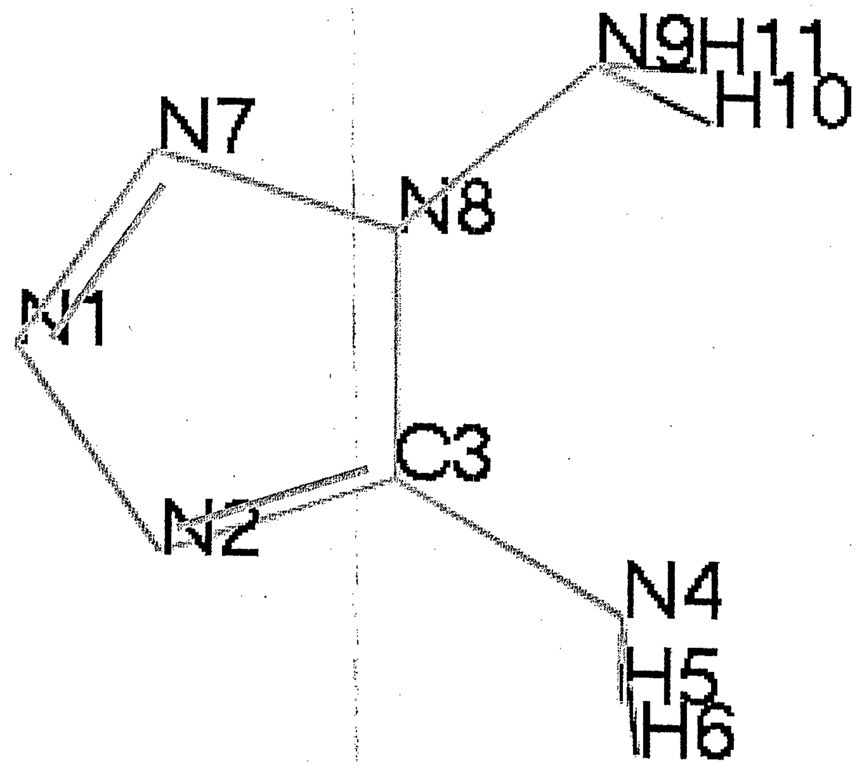
# 1,5-diamino-1,2,3,4-tetrazole

**What is the preferred N-protonation site?**

**What level of theory is required?**

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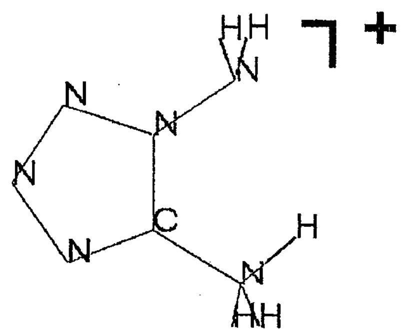
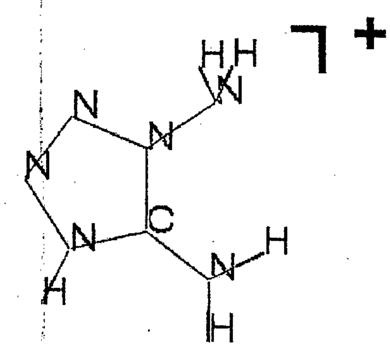
# *B3LYP(3) Structures and Relative Energies (kcal/mol)*

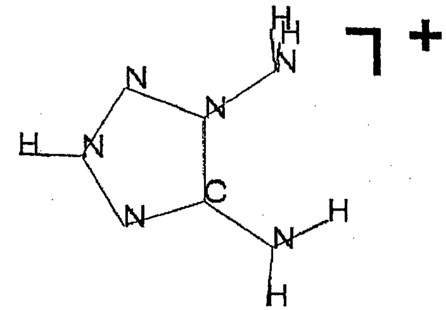
## B3LYP(3)/6-311G(d,p) [B3LYP(3)//aug-cc-pvtz//B3LYP]


1 ($C_s$)

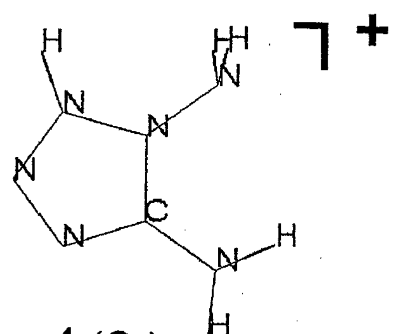
**35.5 [36.6]**


2($C_s$)

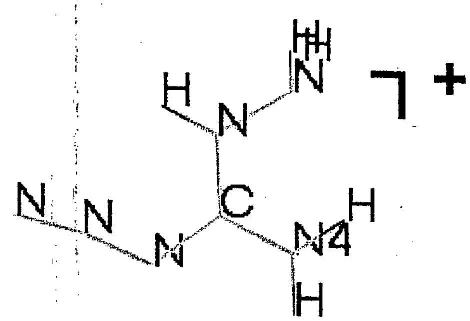
**2.1 [3.2]**


3 ($C_s$)

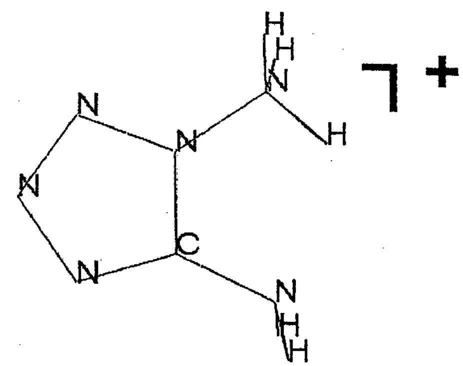
**5.0 [5.6]**


4 ($C_s$)

**18.0 [18.6]**


5($C_s$)

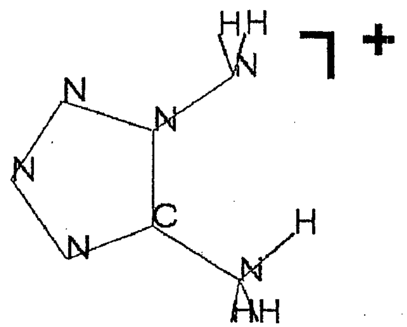
**0.0 [0.0]**


6 ($C_S$)

**42.9 [43.9]**

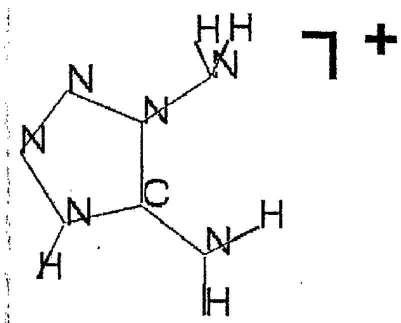
# MP2 Structures and Relative Energies (kcal/mol)

## MP2/6-311G(d,p) [CCSD(T)/6-311G(2df,p)//MP2]



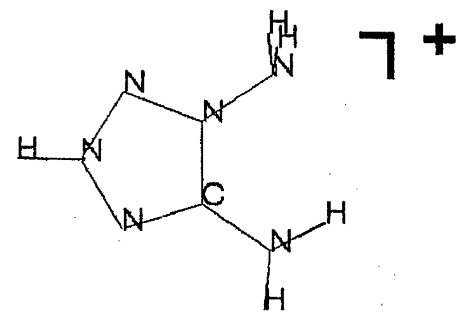
1 ($C_s$)

**26.9 [29.6]**



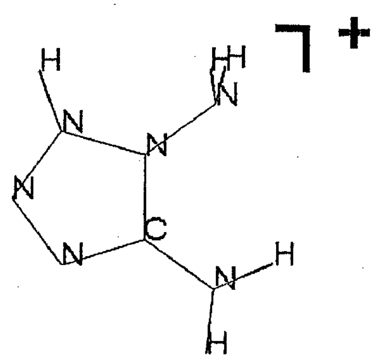
2($C_1$)

**0.6 [0.0]**



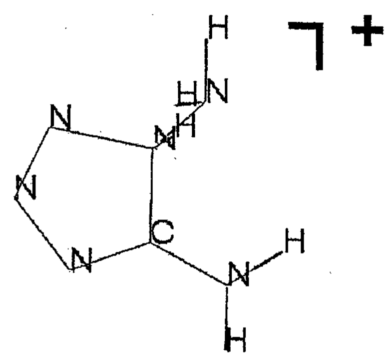
3 ($C_1$)

**0.0 [3.3]**



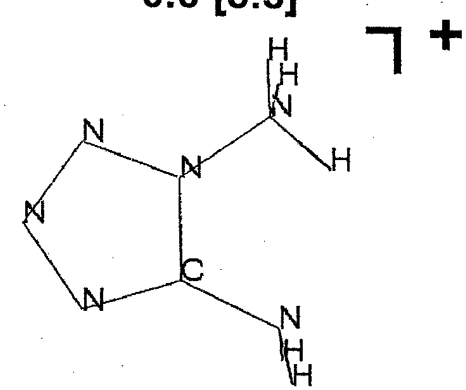
4 ($C_1$)

**18.7 [16.8]**



2($C_1$)

**51.2 [45.6]**



3 ($C_S$)

**36.4 [38.0]**

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# Summary of Relative Energies (kcal/mol)

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| B3LYP(3)/6-311G(d,p) | 35.5 | 2.1 | 5.0 | 18.0 | 0.0 | 42.9 |
| B3LYP(3)/6-311G(2df,p)// | TBD | | | | | |
| B3LYP(3)/aug-cc-pvtz// | 36.6 | 3.2 | 5.6 | 18.6 | 0.0 | 43.9 |
| MP2/6-311G(d,p) | 26.9 | 0.6 | 0.0 | 18.7 | 51.2 | 36.4 |
| MP2/6-311G(2df,p)// | TBD | | | | | |
| MP2/aug-cc-pvtz// | TBD | | | | | |
| CCSD(T)/6-311G(2df,p)//MP2 | 29.6 | 0.0 | 3.3 | 16.8 | 45.6 | 38.0 |

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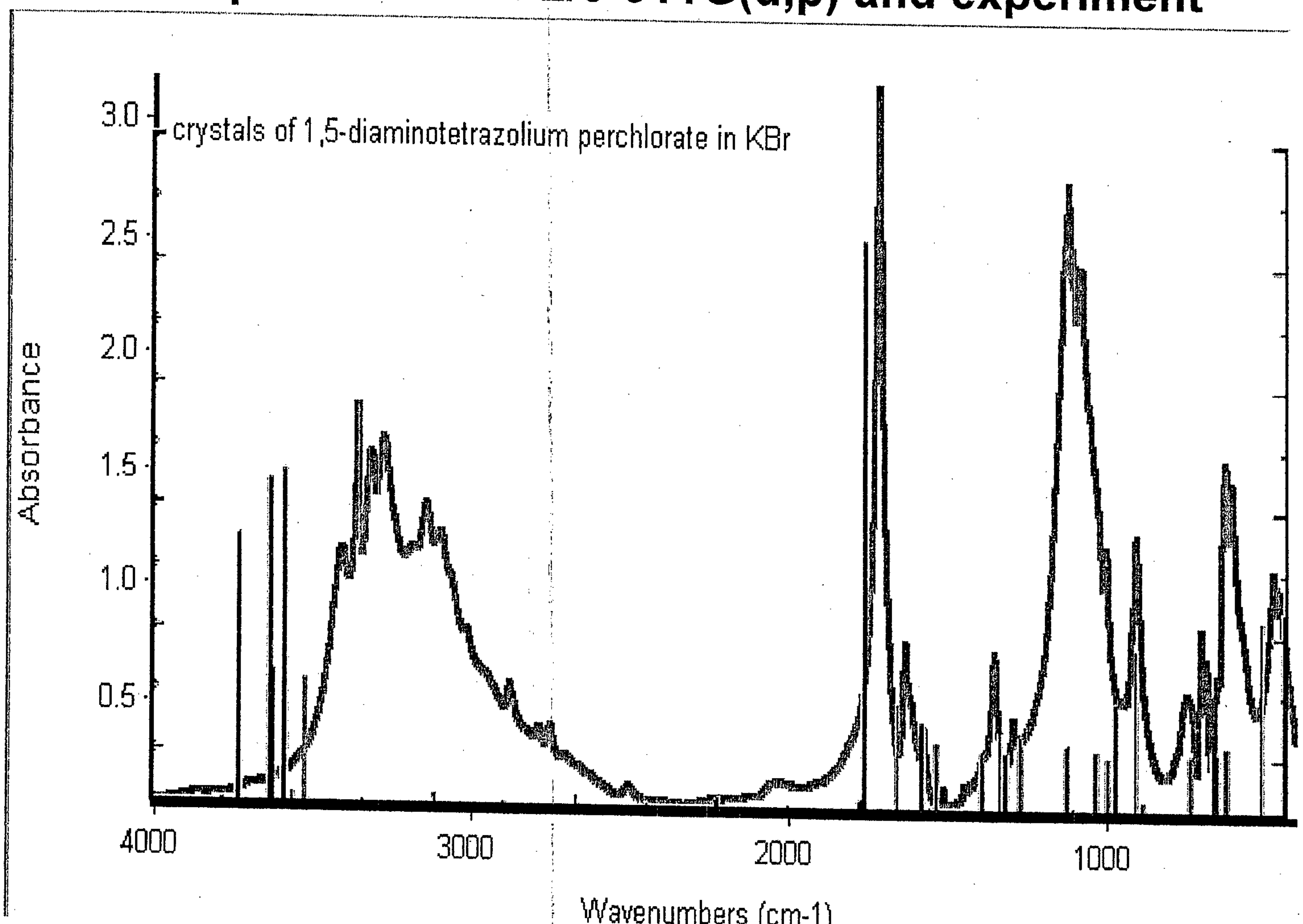
# Infrared Vibrational Spectra

## Comparison of MP2/6-311G(d,p) and experiment

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# Summary & Conclusions

- The structures and relative energies of the six possible N-protonated structures of the 1,5-diamino-1,2,3,4-tetrazolium cation have been computed at the B3LYP(3)/6-311G(d,p) and MP2/6-311G(d,p) levels of theory. Relative energies have been refined at the B3LYP(3), MP2, and CCSD(T) levels, using the 6-311G(2df,p) and aug-cc-pvtz basis sets.

- Isomers 2 (4H) and 3 (3H) are essentially degenerate at all levels of theory.

- B3LYP predicts isomer 5 (1H) to ring open to form an azide $(NH_2NHC(N_3){=}NH_2$.

- CCSD(T)/6-311G(2df,p)//MP2/6-311G(d,p) calculations predict structure 2 to be the most stable isomer, in agreement with the X-ray crystal structure of the perchlorate salt.

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**Common HPC Software Support Initiative**


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